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DYNAMICS OF THE REDOX STATE OF THE MELT IN THE CONTINUOUS PRODUCTION OF CLEAR GLASS

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The effect of a set of external factors on the redox equilibrium of iron and sulfur, changes in melt properties, and light transmission of clear sheet glass is investigated for continuous production of glass. A quantitative estimate of trends in the variations of the redox potential of glass melt is proposed. Practical measures improving the efficiency of a tank furnace by correcting the oxidation state of the melt are considered.

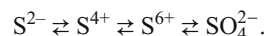
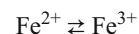
A prompt response to problems of stabilizing the glass-melting process in continuous production is an essential factor in producing high-quality products. This is especially important in the case of significant changes occurring in the process, such as a modification of the batch : cullet ratio or the glass compositions, using different grades of materials, etc. These modifications result in the process parameters going beyond the technological standards. As a consequence, glass quality is often impaired and the production volume decreases.

The experience shows that in carrying out the above specified works it is important to adequately estimate the current situation and to use various techniques to stabilize the prescribed redox potential (ROP) of the glass melt. Note that such technological situations cannot be to a full extent simulated in the laboratory conditions in view of their complexity; therefore, laboratory results, as a rule, differ perceptibly from data obtained in continuous industrial furnaces. Therefore, it is necessary to study in detail the regularities of the variations of the redox state and technological properties of glass melt in continuous production.

The factors influencing the glass melt in continuous production can be arbitrarily divided into two groups:

- staff-controlled systems (hereafter “controlled” systems); they include the batch ROP, the chemical composition (basicity) of the glass, the furnace temperature conditions, and the gas : air ratio;
- uncontrollable factors, such as variations in the granulometric composition of materials, fluctuations in composition of gas-air mixtures fed to the furnace for combustion, and uncontrolled impurities brought by materials, i.e., iron from refractories and sulfurous compounds from the fuel.

As a rule, uncontrolled factors in practical glass melting are neglected due to their diversity and narrow variation limits; the lack of statistical data due to irregular or lacking monitoring of these factors aggravates the problem. We should especially stress the impurities of the variable-valence elements (VVE), namely iron (*d* element) and sulfur (*p* element) coexisting in the melt in the state of the redox equilibrium [1]:



Laboratory studies of silicate glasses of a simple composition have demonstrated that the ratio between the oxidized and the reduced forms of these variable-valence elements may vary within wide limits and is closely related to the controlled factors of the first group. A decrease in the batch ROP, and increase in melting temperature, a decrease in glass basicity, or transition from the oxidizing atmosphere to the reducing one [1] shifts the VVE equilibrium toward their lower valence or vice versa.

The redox reactions modify some technological properties of melts and spectral characteristics of glass [1, 2]. For instance, the presence of perceptible quantities of sodium sulfate in a batch is responsible for the stratification of the glass melt into two liquids that are immiscible at high temperatures. Sulfuric anhydride SO_3 is highly soluble in the melt and behaves as an oxidizer, a clarifier, and a surfactant. Sulfurous anhydride SO_2 in fact does not dissolve in the melt and has reducing properties. As for sulfur-bearing compounds of other metals, data on their effect on glass melt properties in the literature are scarce and contradictory.

Iron, which is a *d* element in the Mendeleev periodic table of elements, exhibits the following spectral absorption

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TABLE 1

Parameter	Technological process characteristics									
	Furnace No. 1, stage		Furnace No. 2, stage				Furnace No. 3, stage			
	1A	1B	2A	2B	2C	2D	3A	3B	3C	3D
Batch components:										
feedstock	Traditional	Nontraditional	Concentrated	Traditional	Local		Traditional		New	
reducing agent	Coal	None	None	None	Coal	Coal	Coal	Coal	Coal	Coal
catalyst	None	"	"	"	None	None	None	None	Na ₂ SiF ₆	Na ₂ SiF ₆
clarifying agent	Na ₂ SO ₄	None	Na ₂ SO ₄ , As ₂ O ₃	Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄	Na ₂ SO ₄
weight content of cullet, %	30	100	30	30	30	30	30	30	30	30
Weight content in glass, %:										
determined in synthesis:										
SiO ₂ + Al ₂ O ₃	73.6	73.6	73.6	73.6	73.6	73.6	74.8	73.5	73.5	73.5
Me ₂ O + MeO	25.9	25.9	25.9	25.9	25.9	25.9	24.3	25.9	25.9	25.9
determined in analysis:										
Fe ₂ O ₃ (total)	0.118	0.178	0.054	0.073	0.180	0.161	0.060	0.071	0.062	0.064
SO ₃ (total)	0.380	0.270	0.410	0.440	0.420	0.450	0.500	0.400	0.350	0.380
Batch ROP*	16.8	No data	19.53	19.20	15.30	18.90	11.72	9.09	15.06	19.30
Fraction of Fe ²⁺ = (Fe ²⁺) × 100/(Fe ²⁺ + Fe ³⁺), %	30.1	40.0	16.1	33.5	38.1	35.1	25.5	37.5	48.8	44.0 – 46.0
Melting temperature, °C	1500	1515	1510	1520	1560	1640	1470	1510	1530	1500
CO content in furnace atmosphere, vol. %	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Light transmission, %	85.0	74.0	89.2	86.8	77.4	87.4	88.4	86.8	84.5	Not determined

* The batch ROP was calculated based on the data in [1].

bands: bivalent iron — in the red spectrum with a maximum around 1100 nm and trivalent iron — in the violet spectrum [1, 2]. The maximum flame and furnace roof radiation corresponds to approximately 1100 nm [1]; therefore, the reduced form Fe₂ decreases the diathermancy of the melt, impairs the transfer of thermal radiation into the glass melt depth, impedes melting, clarification, and homogenization, and impairs the homogeneity of glass [3]. Trivalent iron has an opposite effect.

At the same time, a glass melt in industrial melting experiences a simultaneous impact of several factors that have an opposite effect on the redox equilibrium. Therefore, the result of their combined impact on the VVE and glass melt properties is difficult or even impossible to predict.

The purpose of the present paper is to study the joint effect of external factors on the variation of the redox equilibrium of the VVE and to quantitatively estimate the transformation of the redox states in a clear glass melt (the glass melt ROP) in industrial production.

We investigated glass-melting tank furnaces of similar design with lateral flame direction and rated capacity ranging from 75 to 160 tons of glass melt per day. Table 1 lists some quantitative parameters of the technological processes considered.

According to the known principle of the theory of acids and bases in silicate melts [1, 4] regarding the correlation between the acid-base processes (reactions between the basic

glass components: SiO₂, Al₂O₃, MeO, Me₂O) and the redox processes (reactions between the variable-valence impurity oxides), we used the glass basicity indicator [3], i.e., the fraction of bivalent iron, for the quantitative estimate of changes in the oxidation state of the melt (glass melt ROP). The increase in this fraction indicates a decreased oxidizing (increased reducing) potential of the glass melt, and vice versa:

$$d_{\text{Fe}^{2+}} = \frac{C_{\text{Fe}^{2+}}}{C_{\text{Fe}^{2+}} + C_{\text{Fe}^{3+}}} \times 100,$$

where $C_{\text{Fe}^{2+}}$ and $C_{\text{Fe}^{3+}}$ is the weight content of bivalent and trivalent iron in glass converted to metal, %.

This parameter makes it possible to analyze the combined effect of all factors and estimate the trend in the variation of the glass melt ROP.

The process in tank furnace No. 1 instead of traditional materials (stage 1) uses technological waste, namely cullet and erclaise (stage 1B). This substitution was expected to decrease the temperature and facilitate melting, since cullet is fully formed glass and, unlike the batch, does not contain low- or high-melting components. In fact we observed a contrary effect: the melting zones were extended, the amount of gaseous and crystalline inclusions in the glass ribbon grew, and the light transmission of glass significantly deteriorated,

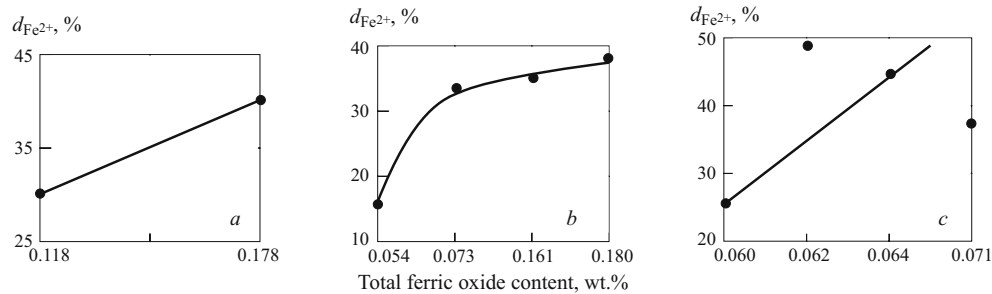


Fig. 1. Variation in the fraction of ferrous iron $d_{\text{Fe}^{2+}}$ on the total Fe_2O_3 content ion glass for system Nos. 1 (a), 2 (b) and 3 (c).

since the glass melt acquired a golden-brown tint. Table 2 shows the effect of each individual factor and analyzes their combined effect on $d_{\text{Fe}^{2+}}$ and the ROP of the glass melt.

In furnace No. 2 an intense oxidizer As_2O_3 was removed from the batch (stages 2A and 2B); at the same time the concentrated material was replaced by the traditional and local materials (stages 2A – 2C).

In system No. 3 the glass composition was corrected toward a lower viscosity (stages 3A and 3B) and the raw materials were replaced (stages 3B and 3C).

Analysis shows that several factors in furnaces Nos. 1 – 3 have significant influence on the equilibrium of the valence forms of the VVE and the glass melt ROP. This is clearly seen from the data in Table 2. Of all factors listed in this table the following ones contribute to increasing $d_{\text{Fe}^{2+}}$ and, accordingly, decreases the glass melt ROP:

- increase in the content of cullet in glass;
- increased melting temperature;
- increased CO concentration in the furnace atmosphere;
- decreased quantity of clarifiers (sodium sulfate, arsenic oxide)
- decrease in the batch ROP.

An increase in the matrix basicity (content of $\text{Me}_2\text{O} + \text{MeO}$) and the mass content of iron in glass decreases $d_{\text{Fe}^{2+}}$ and increases the oxidizing potential of the melt.

It is evident that the majority of the factors (four out of five, i.e., 80% in System No. 1 and three out of four, i.e., 75% in system No. 2) increase the fraction of ferrous iron and raise the reducing potential of the melt; consequently, under their combined effect the ROP of the glass melt in both systems decreased.

In system No. 3 three out of the four external factors (75%) at stages 3A and 3B and two out of four (50%) at stages 3B and 3C increase $d_{\text{Fe}^{2+}}$. The rest of the factors have the opposite effect. However, a perceptible increase in the reducing potential of the glass melt was observed at stages 3B and 3C as well.

Figure 1 shows the dependences of the reduced iron fraction $d_{\text{Fe}^{2+}}$ on the total weight content of Fe_2O_3 in glass. We

can see that in all cases considered the combination of external factors strictly increases $d_{\text{Fe}^{2+}}$, therefore, the oxidizing potential of the melt actually decreases. It should be noted that the substantial dispersion of the points in Fig. 1c is due to the presence of a melting catalyst, namely sodium silicofluoride in the batch (stages 3C and 3D), which significantly increases the fraction of Fe^{2+} in the glass melt [8].

The dynamics of the glass ROP variations at each stage can be quantitatively estimated based on the increment of the

TABLE 2

External factor	Variation of $d_{\text{Fe}^{2+}}$	
	predicted based on published data	actual in transition from stage A to stage B
<i>System No. 1 (stages 1A, 1B)</i>		
Replacing batch by cullet	Increase [5]	Increase: 30.1 – 40%
Decrease in SO ₃ content	Increase [1]	
Raising melting temperature	The same	
Increase in CO content in furnace atmosphere	"	Increase: 16.0 – 33.5 – 38.1%
Increase in content of ferrous compounds	Decrease [6]	
<i>System No. 2 (stages 2A – 2B)</i>		
Removal of oxidizer As ₂ O ₃	Increase [1]	Increase: 25.5 – 37.6%
Decrease in batch ROP	The same	
Raising melting temperature	"	
Increase in content of ferrous compounds	Decrease [6]	Increase: 37.5 – 48.8%
<i>System No. 3 (stages 3A – 3B)</i>		
Raising melting temperature	Increase [1]	Increase: 37.5 – 48.8%
Decrease in batch ROP	The same	
Increase in content of ferrous compounds	Decrease [6]	
Increase in glass basicity	Decrease [1]	Increase: 37.5 – 48.8%
<i>System No. 3 (stages 3B, 3C)</i>		
Introduction of melting catalyst Na ₂ SiF ₆	Increase [7]	Increase: 37.5 – 48.8%
Raising melting temperature	Increase [1]	
Decrease in content of ferrous compounds	Increase [6]	
Increase in batch ROP	Decrease [1]	

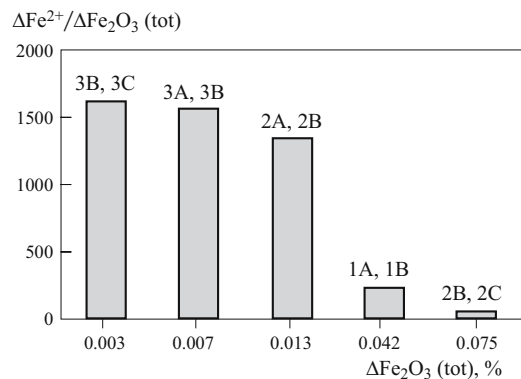


Fig. 2. The ratio of the increase in the fraction of ferrous iron to the variation of total ferric oxide content in glass.

ferrous iron fraction in relation to the change in the total iron

$$\text{oxide content} \left(\frac{\Delta d_{\text{Fe}^{2+}}}{\Delta \text{Fe}_2\text{O}_3 (\text{total})} \right).$$

The results of the calculations are given in Table 3 and in Fig. 2.

The most significant variation of the redox state of the melt was registered in systems No. 2 (stages 2A, 2B) and No. 3 (stages 3A – 3B, 3B – 3C) in the range of a relatively low content of Fe_2O_3 in glass ranging from 0.054 to 0.073%. Increasing the content of ferric oxide above 0.08% in furnaces No. 1 (stages 1A, 1B) and No. 2 (stages 2B – 2C) significantly decelerates the growth rate of the glass melt ROP.

TABLE 3

Parameter	Comparable stages				
	1A, 1B	2A, 2B	2B, 2C	3A, 3B	3B, 3C
$\Delta d_{\text{Fe}^{2+}}$	9.9	17.5	4.6	12.5	11.3
$\Delta \text{Fe}_2\text{O}_3 (\text{total})$	0.042	0.013	0.075	0.003	0.007
$\frac{\Delta d_{\text{Fe}^{2+}}}{\Delta \text{Fe}_2\text{O}_3 (\text{total})}$	236	1346	61.3	1562	1614

TABLE 4

Stage	Content of Fe^{2+} , wt. %	Light transmission, %, per 1 cm glass thickness
1A	0.025	85.0
1B	0.050	74.0
2A	0.006	89.2
2B	0.017	86.8
2C	0.048	77.4
2D	0.040	87.4
3A	0.011	88.4
3B	0.019	86.8
3C	0.021	84.5
3D	0.020	Not determined

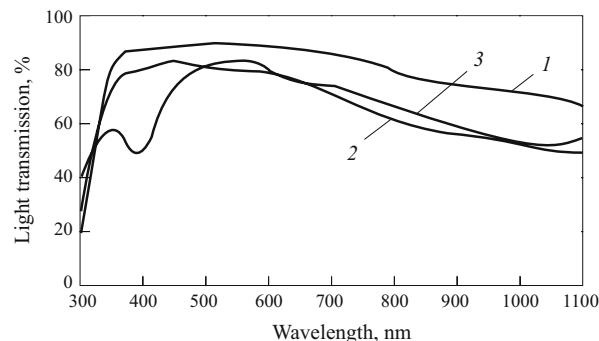


Fig. 3. Spectra light transmission curves of glass samples of 1.5 mm obtained at stages 2A (1), 2B (2), and 1B (3).

Table 4 correlates the light transmission of glasses in the visible spectrum with their absolute mass content of bivalent iron.

It can be seen that the light transmission of glass is proportional to its content of ferrous iron. This agrees with the data in [1].

Figure 3 shows the spectral curves of light transmission in glasses with different ROP levels produced in systems No. 1 and No. 2. The glass produced at stage 2A contains the intense oxidizer As_2O_3 , therefore, the fraction of Fe^{2+} here is minimal and equal to 16.1%, whereas the light transmission is maximal (89.2%). The glass produced at stage 2C, as opposed the glass melted at stage 2A, has no arsenic oxide in the batch and a higher content of iron in the batch and in the glass. As a consequence, the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ equilibrium shifts to the left, the fraction of Fe^{2+} reaches 38.1%, and the light transmission decreases to 77.4%; accordingly, curve 2 is positioned below curve 1 (Fig. 3). Stage 1B has even more intense reducing conditions than stage 2C. This is corroborated by the presence of CO in the furnace atmosphere, the content of SO_3 decreasing to a minimal value, and the emergence of the absorption band in the spectral curve near 400 – 410 nm, which corresponds to the formation of iron sulfide and the golden-brown tint in glass. The fraction of bivalent iron at stage 1A grows to 40%.

Since the continuous glass-melting process restricts the possibilities of varying the temperature and gas conditions, the method of chemical intensification of glass melting was used in furnaces Nos. 2 and 3 to prevent the negative effect of the shift in the VVE redox equilibrium [3]. At stage 2D the sodium sulfate : coal ratio was optimized. This brought the fraction of ferrous iron from 38.1 to 35.1%, increased the diathermancy of the melt, and lowered the melting temperature from 1540 to 1520°C. At stages 3C and 3D we introduced Na_2SiF_6 into the batch, which decreases the viscosity and surface tension of the glass melt [5]; accordingly, the ROP of the batch increased. Altogether this combination decreased the fraction of Fe^{2+} from 48.8 to 46 – 44% and the melting temperature from 1530 to 1500°C.

Thus, the ROP of a glass melt in continuous production constantly changes due to the combined effect of numerous

external factors. As a result, the redox equilibrium of variable-valence impurity elements shifts and the technological properties of the melt change. This disturbs the stability of glass melting and impairs the product quality.

The quantitative estimate of the melt ROP variation for clear glasses using the indicator

$$d_{\text{Fe}^{2+}} = \left(\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Fe}^{3+}} \right) \times 100$$

provide an objective assessment of the actual change in the glass melt ROP and makes it possible to undertake prompt measures to stabilize the glass-melting process.

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